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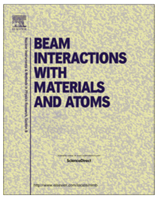

# The application of phase contrast X-ray techniques for imaging Li-ion battery electrodes

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ABSTRACT

In order to accelerate the commercialization of fuel cells and batteries across a range of applications, an understanding of the mechanisms by which they age and degrade at the microstructural level is required. Here, the most widely commercialized Li-ion batteries based on porous graphite based electrodes which de/intercalate $Li^+$ ions during charge/discharge are studied by two phase contrast enhanced X-ray imaging modes, namely in-line phase contrast and Zernike phase contrast at the micro (synchrotron) and nano (laboratory X-ray microscope) level, respectively. The rate of charge cycling is directly dependent on the nature of the electrode microstructure, which are typically complex multi-scale 3D geometries with significant microstructural heterogeneities. We have been able to characterise the porosity and the tortuosity by micro-CT as well as the morphology of 5 individual graphite particles by nano-tomography finding that while their volume varied significantly their sphericity was surprisingly similar. The volume specific surface areas of the individual grains measured by nano-CT are significantly larger than the total volume specific surface area of the electrode from the micro-CT imaging, which can be attributed to the greater particle surface area visible at higher resolution.

## 1. Introduction

“Electrochemical device” is a term used to describe a group of technologies including fuel cells, batteries, electrolysers, and super-capacitors. Whilst many of these technologies are already in common daily usage (for example Li-ion batteries in consumer electronics), in the future electrochemical devices will play an increasing role in our lives – from fuel cells that can power our homes to high performance batteries for our cars. These devices will play a key role in reducing our carbon footprint and improving security of energy supply. In spite of progress in recent years, further improvements in durability and performance are required to enable the application of these devices across a range of applications.

Electrochemical reactions in all of these devices are supported by porous materials, which need to combine a range of functions including mass transport and catalysis; whilst the balance of these will vary between devices, there is a common link between the microstructure of the materials and its performance in the devices. Currently, the relationship between microstructure and performance in electrochemical devices is poorly understood; this is compounded by the fact that, during processing and operation, the microstructure is liable to physically alter (microstructural evolution) causing degradation of the whole device. Understanding the broad range of physical phenomena occurring in these porous materials is paramount to improving device performance and lifetime [1–3].

In lithium ion batteries, reactions occur between porous cathode materials, which act as a Li source – such as $LiFePO_4$, $LiCoO_2$ and $LiMn_2O_4$, and anode materials which act as a Li sink – most commonly graphite (or an alternative carbon derivation) is utilised, which can intercalate $Li^+$ ions within its galleried structure. These porous electrode microstructures are flooded with ionically conducting electrolyte (commonly $LiPF_6$); Fig. 1(A) shows a schematic of a battery during charge, where $Li^+$ ions originally present in the positive electrode and electrolyte are intercalated into the bulk material of the negative electrode.

The electrode is comprised of a number of phases: the active material, conductive additive, binder, and solid electrolyte interphase (SEI)

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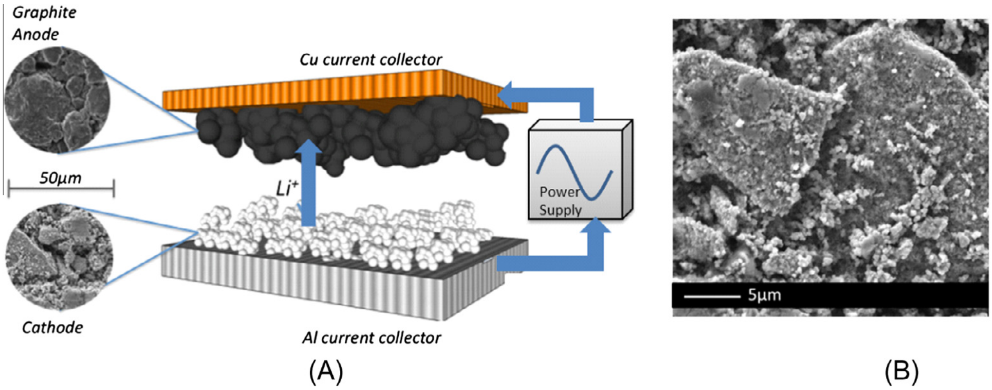

**Fig. 1.** (A) Schematic of Li-ion battery during charging (B), scanning electron micrograph of an $LiMn_2O_4$ cathode material demonstrating its complex microstructure [5].

layer. Fig. 1(B) shows an electron micrograph of a composite battery electrode, revealing its complex 3D structure. These porous electrode microstructures are expected to support a range of physical phenomena which can be linked to device level performance; for example, a nano-structured material with high volume specific surface area may provide rapid de/intercalation of Li-ions to promote fast rate charge/discharge. However, this rate capability may be obtained at the expense of overall battery capacity, which would require larger bulk particles to maximize the quantity of intercalated Li [4].

Historically, the role of electrode microstructure in determining the macroscopic performance of Li-ion batteries has not been well understood. For example, the macro-homogenous model of Newman and co-workers [6] has been extremely successful in predicting battery performance; however, its ability to predict battery degradation and failure has been more limited [1] – microstructurally driven degradation is acknowledged to be a leading cause of battery performance loss, and therefore a combination of accurate image data with relevant simulation tools would greatly improve our understanding of these processes [7].

Recently, the application of tomography tools (primarily using X-rays and focused ion beam imaging) has revolutionized understanding of the microstructure of electrochemical devices [8–10], and has been applied to explore a range of battery electrode materials [11–13] providing unprecedented insight into the detail of real-life electrode geometries.

Multi length-scale X-ray imaging is a powerful tool to explore the often hierarchical structure of Li-ion battery electrodes from the particle [3] to the device [14] length scale. Recently published results using different X-ray CT platforms demonstrate that the choice of resolution and representative volume vary significantly depending on the parameter under investigation [3]. For battery electrodes it has been shown that the resolution requirements for bulk porosity calculation are not as stringent as for surface area quantification [3]. In the current case a relatively coarse resolution can be used so as to gain the statistical sampling advantages of interrogating a larger volume without compromising the accuracy of the porosity measurement.

However surface area calculations, which are sensitive to small variations in surface roughness, require higher resolution imaging. In order to provide a comprehensive description of these electrodes, it is therefore important to understand their structures at multiple length scales. Whilst this has been demonstrated for $LiMn_2O_4$ cathode materials [3], for graphite based anode materials the limitations of conventional imaging modalities are prohibitive: the interaction of typical $Ga^+$ focused ion beam with graphite structures leads to highly non-uniform milling, thereby limiting the application of FIB-SEM 3D imaging techniques. Similarly, the use of absorption contrast X-ray CT is limited due to the low attenuation of the incident (lab or synchrotron) X-ray beam by low atomic number materials, such as carbon.

The application and proliferation of phase contrast X-ray imaging techniques is increasingly widespread, as evidenced by the recent Royal Society Discussion Meeting “Taking X-ray Phase Contrast Imaging Into Mainstream Applications” [15]. In order to demonstrate the potential of this technique to explore low atomic number materials (predominantly graphite) that are commonly found in Li-ion batteries, here we demonstrate the use of both in-line propagation and Zernike X-ray phase contrast imaging. This study demonstrates the application of X-ray phase contrast imaging to understand the structure of graphite electrodes at two length scales, whilst a larger systematic study is required to comprehensively catalogue and compare the full range of possible electrode materials, here we present for the first time a methodology by which reliable multi length scale investigations can be facilitated.

## 2. Techniques

Graphite anodes from Li-ion batteries have been obtained from commercial suppliers and have been characterized using two tomography platforms: the first is the microCT end station at the TOMCAT Beamline at Swiss Light Source, which provides absorption and phase contrast imaging with an isotropic voxel size ranging from 0.16 to 14.8 µm (field of view from 0.42 × 0.35 to 30 × 30 $mm^2$, respectively) across an energy range of 8–45 keV [16].

The second is the laboratory-based Xradia nanoXCT-100 X-ray microscope: the unique architecture of the Xradia instrument utilizes a capillary condenser lens to focus the incident X-ray beam and a Fresnel zone plate objective lens for post transmission focusing. Fresnel zone plates are diffraction based lenses that, in this instrument, provide sub-100 nm imaging resolution across a fixed field of view from 15 × 15 to 65 × 65 $\mu m^2$. The lab tool operates using a rotating anode Cu source with a quasi-monochromatic 8 keV photon energy. Schematics of both instruments are shown in Fig. 2.

To accurately image these carbon samples, two X-ray phase contrast modalities were applied which were particularly appropriate for imaging low-attenuation materials. On the TOMCAT beamline at the Swiss Light Source an in-line propagation phase contrast technique was employed, which does not require any X-ray optics to be positioned between sample and detector. As X-rays pass through a specimen, both amplitude reduction and phase modulation occur as described by the complex refractive index of the media, resulting in both attenuation and refraction of the beam. When the incident and refracted waves propagate